



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 218 245 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: 15.05.91 (51) Int. Cl.<sup>5</sup>: **B65D 65/38, B29C 49/00, C08L 67/02, //(C08L67/02, 31:04),(C08L67/02,23:08)**
- (21) Application number: **86113929.3**
- (22) Date of filing: **08.10.86**

(54) Injection stretch blow container.

(30) Priority: **09.10.85 JP 225661/85**

(43) Date of publication of application:  
**15.04.87 Bulletin 87/16**

(45) Publication of the grant of the patent:  
**15.05.91 Bulletin 91/20**

(94) Designated Contracting States:  
**BE DE FR GB IT NL SE**

(56) References cited:  
**EP-A- 0 019 438**  
**DE-A- 1 794 036**  
**GB-A- 2 011 443**  
**US-A- 4 410 482**

**DERWENT JAPANESE PATENT GAZETTE,**  
week 8534, class A, 2nd October 1985, page  
7, section CH, no. 85-206106, Derwent Pub-  
lications Ltd, London, GB; & JP-A-60 129 256  
(NIPPON SYNTHESIS CHEMICAL INDUS-  
TRIES) 10-07-1985

(73) Proprietor: **KURARAY CO., LTD.**  
**1621 Sakazu**  
**Kurashiki-City Okayama Prefecture 710(JP)**

(72) Inventor: **Moritani, Tohei**  
**2-2-34, Showa**  
**Kurashiki-City(JP)**  
Inventor: **Kawai, Syuji**  
**3-5, Height**  
**Kurashiki-City(JP)**  
Inventor: **Shimamura, Kunihiro**  
**2-3-50, Nakai-Cho**  
**Okayama-City(JP)**  
Inventor: **Sato, Toshiaki**  
**Oji AP 2-301 1660, Sakazu**  
**Kurashiki-City(JP)**

(74) Representative: **Vossius & Partner**  
**Siebertstrasse 4 P.O. Box 86 07 67**  
**W-8000 München 86(DE)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Rank Xerox (UK) Business Services

EP 0 218 245 B1

BEST AVAILABLE COPY

PATENT ABSTRACTS OF JAPAN, vol. 9, no. 215 (M-409)[1938], 3rd September 1985; & JP-A-60 76 325 (MITSUI SEKIYU KAGAKU KOGYO K.K.) 30-04-1985

RESEARCH DISCLOSURE, no. 230, June 1983, page 214, no. 23022, Kenneth Mason Publications Ltd, Emsworth, GB; "Static mixing of laminar barrier polymer blends in multiple head equipment"

MODERN PLASTICS INTERNATIONAL, vol. 14, no. 1, January 1984, page 6, Lausanne, CH; "Novel barrier technology for polyolefin containers"

## Description

The present invention relates to an injection stretch blow container having a high gas-barrier quality due to the laminar structure of the blend of saturated polyester and a saponification product of an ethylene-vinyl acetate copolymer (hereinafter referred to as "EVOH").

In relation to a composition of saturated polyester and EVOH, Japanese Patent Laid-Open No. 20073/1981 discloses one of such compositions, Japanese Patent Laid-Open No. 76325/1985 discloses a biaxially stretched molded product, and Japanese Patent Laid-Open No. 148442/1985 discloses a blow bottle.

When containers are produced by these known methods, the gas barrier quality is improved if the amount of EVOH is less than about 30 wt %, but the degree of improvement is too low to be satisfactory in terms of enhancement of the preservability of foodstuffs. This will be clear from Comparative Example 1 which will be later described. On the other hand, if the amount of EVOH is increased in order to improve the preservability, the moldability in stretch blow is reduced. Thus, it is difficult to produce the intended gas-barrier container. For these reasons, no container made of a composition of saturated polyester and an EVOH has yet been put to practical use. It is known that a container having a high gas-barrier quality is obtained by laminating saturated polyester and an EVOH by using a co-extrusion technique, but this method has not been put to practical use either because of high molding cost.

Accordingly, it is an object of the present invention to eliminate the above-described problems in the prior art and to provide an injection stretch blow container having a high gas-barrier quality due to the laminar structure of the blend of saturated polyester and an EVOH.

To achieve this aim, the present invention injection stretch blow container comprising a combination of 97 to 70 parts by weight of saturated polyester and 3 to 30 parts by weight of a saponification product of an ethylene-vinyl acetate copolymer, having many areas at least at the body wall portion of said container in each of which areas substantially two-dimensional thin layers of said saponification product of said ethylene-vinyl acetate copolymer are laminated in parallel to the wall surface of said container in a matrix of saturated polyester, said saponification product of said ethylene-vinyl acetate copolymer in said area (20 x 20  $\mu$ m; vertical section or longitudinal section of the body wall of said container) having 0.001 to 1  $\mu$ m in average thickness and at least 5 in average aspect ratio, and the laminated structural index represented by the following formula being at least 5:

Laminated structural index

$$I = (1 / n) \sum_{i=1}^n (L_i / h_i),$$

wherein  $L_i$  represents a length of the overlapped portion of adjacent layers of the saponification product of the ethylene-vinyl acetate copolymer, and

$h_i$  represents a distance between adjacent layers of the saponification product of the ethylene-vinyl acetate copolymer.

No container having the above-described structure has been obtained by the methods disclosed in the prior-art literatures. A container of the present invention is very useful for packaging foods in a wide range including carbonated beverage, because it has a high gas barrier quality which is equivalent to that of a laminate obtained by the co-extrusion of saturated polyester and the EVOH.

The following description of the preferred embodiments of the present invention is taken in connection with the accompanying drawings.

As examples of saturated polyester resins which are used in the present invention, the following polymers will be cited: poly (ethylene terephthalate) (PET), poly (butylene terephthalate), poly (ethylene terephthalate/isophthalate), and poly (ethylene glycol/cyclohexanedimethanol/terephthalate).

In addition, the above described polymers which contain the following copolymerization components are also usable: diols such as ethylene glycol, cyclohexane dimethanol, neopentyl glycol and pentanediol; dicarboxylic acids such as isophthalic acid, benzophenonedicarboxylic acid, diphenylsulfone dicarboxylic acid, diphenylmethane dicarboxylic acid, propylene bis (phenylcarboxylic acid), diphenylsulfone dicarboxylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and diethyl succinic acid. Among these, poly (ethylene terephthalate) is usually preferable for achieving the aim of the present invention, and poly (ethylene terephthalate/isophthalate) containing 2 to 12 mol% of isophthalate in a monomer of the acid component is also preferable due to the

easiness of molding and the excellent gas-barrier property of a container obtained. The intrinsic viscosity of saturated polyester is not specified, but is preferably 0.5 to 1.4 dl/g, more preferably 0.6 to 0.9 dl/g.

The saponification product of ethylene-vinyl acetate copolymer (EVOH) in the present invention may be any product that is obtained by hydrolyzing the vinyl acetate unit of a copolymer of ethylene and vinyl acetate, but, in particular, a product which contains 25 to 60 mol% of ethylene unit, the degree of saponification of which is at least 96 % and the melt index (at 190 °C, 2160 g) of which is in the range of 0.2 to 60 g/10min. is preferable. As a result of the production of containers of the present invention using various kinds of EVOHs, an unexpected fact has been found that a blend composition produced using an EVOH containing 37 to 50 mol % of ethylene unit exhibits a propensity of forming a laminar structure in the wall material of the container, thereby displaying a high gas-barrier quality and excellent injection stretch blow moldability. Since an EVOH which has an especially high gas-barrier quality contains 28 to 36 mol% of ethylene, it can be said this fact is a least expected result. The EVOH in the present invention may be modified by a comonomer of less than 5 mol%. Such a modifying monomer will be exemplified by propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, acyclic ester, methacrylate ester, maleic acid, fumaric acid, itaconic acid, higher fatty acid vinyl ester, alkyl vinyl ester, N-(2-dimethylaminoethyl) methacrylamides or their quaternary monomers, N-vinyl imidazole or its quaternary monomer, N-vinyl pyrrolidone, N-n-butoxymethylacrylamide, vinyl trimethoxysilane, vinyl methyl dimethoxysilane, and vinyl dimethyl methoxysilane.

If the amount of EVOH of a composition of the present invention is less than 3 parts by weight, sufficient gas barrier quality is not obtained even if the EVOH is molded into a laminar structure. If the amount of EVOH exceeds 30 parts by weight, it is difficult to obtain a good laminar molded product. According to a method to produce the container of the present invention, it is not necessary to use such a great amount of EVOH.

In producing a container in accordance with the present invention, a predetermined amount of saturated polyester and EVOH are first blended, preferably by a dry blend method. Pelleting by pre-blending, which is executed in an ordinary polymer blend and which is disclosed in Japanese Patent Laid-Open No. 76325/1985, is not preferable. However, in the case of pelleting by pre-blending while controlling mixture to extremely low level is carried out, it is possible to obtain a container having such a structure as specified in the present invention. In particular, melting and kneading in a multi-axial extruder, kneader, Banbury mixer, etc. cannot produce the container of the present invention, thereby being unfavorable. The size of a resin particle being used has a potent influence of the result. A particle size of less than 0.5 mm is not preferable and it is preferable that the shortest side is between 1 mm and 7 mm in order to obtain a good result.

The thus-dry-blended resin is charged into an extruder, usually, an injection molder provided with a uniaxial extruder, while avoiding additional excessive mixture. It is preferable that this uniaxial extruder has no portion which accelerates mixing such as a mixing screw, DIS screw, and static mixer as a dumbadge, barrier type and pin type screws, respectively, which are generally used in molding polymer blends. The most preferable uniaxial extruder in accordance with the present invention is an extruder which has a simple full-flight type screw having, for example, an LD of 10 to 30 and a compression ratio of 1.2 to 4. The temperature of injection molding is usually 220 to 330 °C, preferably 240 to 280 °C. In order to form an excellent laminar structure disclosed in the present invention, specific injection conditions are required. That is, the rotational speed of the screw must be low to obtain a good effect. It is 20 to 160, preferably 20 to 100 rpm. It is necessary not to retain the blended resin more than 30 minutes at a temperature above 260 °C. If it is retained for more than 30 minutes, it is difficult to form a laminar structure which is characteristic of the present invention, and the stretch blow moldability is reduced. It is necessary that the injection pressure is high (more than 80 kg/cm<sup>2</sup>, preferably 95 kg/cm<sup>2</sup>) and the injection time is short (within 3 seconds, preferably 1.5 seconds). The astonishing fact has been found that the laminar structure is rapidly developed by suddenly cooling the injected resin by lowering the temperature of the mold in advance. A suitable temperature to which the mold is cooled is 5 to 18 °C. In the present invention it is essential to use an injection molder, and even if a molding method which can avoid additional mixture is used, neither compression molding nor extrusion molding (disclosed in Japanese Patent Laid-Open No. 121017/1980) can produce a container having a high gas barrier quality such as those disclosed in the present invention. The parison thus obtained by injection molding is stretch-blown, thereby obtaining a container of the present invention. The parison is enlarges 5 to 20 times, preferably 7 to 15 times by stretch blow at a temperature of 80 to 120 °C, preferably 90 to 110 °C. The thus-obtained container (bottle or the like) is excellent in resistance to shock and resistance to creep as well as gas-barrier quality, and acquires importance as a container for carbonated beverage such as beer and refreshing beverage. In order to bottle carbonated beverage, it is necessary not only to prevent the carbon dioxide gas from escaping through the wall of the container but also to prevent the foodstuff within the container from being oxidized by oxygen

which may permeate the container. The container of the present invention has an extremely high gas barrier quality. The main characteristic of the present invention is that the EVOH among the wall materials of the container has the above-described laminar structure, which particular structure is considered to have brought a container having such a high gas-barrier quality. Accordingly, the container of the present invention is easily distinguished from a container in the prior art in that it has the aforementioned laminar structure. This laminar structure is obtained by the above-described specific injection stretch blow. The formation of the laminar structure is easily confirmed by observing the section of the container by a transmission electron microscope. The container obtained according to the present invention is characterized in that said container has many areas at least at the body wall portion of said container in each of which areas substantially two-dimensional thin layers of said saponification product of said ethylene-vinyl acetate copolymer are laminated in parallel to the wall surface of said container in a matrix of saturated polyester, said saponification product of said ethylene-vinyl acetate copolymer in said area (20 x 20  $\mu\text{m}$ ; vertical section or longitudinal section of the body wall of said container) has 0.001 to 1  $\mu\text{m}$  in average thickness, preferably 0.001 to 0.2  $\mu\text{m}$  and at least 5 in average aspect ratio, preferably at least 15, and the laminated structural index represented by the following formula is at least 5, preferably at least 15.

Laminated structural index

$$I = (1 / n) \sum_{i=1}^n (L_i / h_i),$$

wherein  $L_i$  represents a length of the overlapped portion of adjacent layers of the saponification product of the ethylenevinyl acetate copolymer, and

$h_i$  represents a distance between adjacent layers of saponification product of ethylene-vinyl acetate copolymer.

At least the body portion of the container must have many of such areas and the shoulder portion, neck portion, and bottom of the container need not necessarily have that structure.

Although an injection-molded container which is formed solely of a composition of saturated polyester and an EVOH has been mainly explained in the above, a multi-layered injection-molded container which contains a saturated polyester layer (P) in addition to the blend layer (B) is included in the scope of the present invention. The structure of the layer in this case is preferably P / B (outer layer), B / P (outer layer), or P / B / P, and it is usually unnecessary to use a bonding resin.

It is possible to add another thermoplastic resin, antioxidant, pigment, filler, nucleating agent, etc., to the composition of the present invention in the range which does not impair the object of the present invention.

The present invention will be explained in more detail with reference to the following examples.

#### Example 1

90 parts of pellets (size: 2 x 2 x 4 mm) of polyethylene terephthalate (hereinafter referred to as "PET") having an intrinsic viscosity of 0.80 dl/g were dried under a reduced pressure so as to have a water content of not greater than 50 ppm. 10 parts of pellets (size: 2 x 3 x 4 mm) of an EVOH in which ethylene units were 44 mol %, the degree of saponification was 99 % and the melt index (at 190 °C, 2160 g) was 5g/10 min were dried under a reduced pressure so as to have a water content of not greater than 200 ppm. A stretch bottle blower having an extruder with a built-in full-flight screw (L/D : 20, diameter: 36 mm, effective length: 720 mm, compression ratio: 2.5) was prepared. After dry blending both pellets, they were injected into a mold which was provided with an injection gate having a diameter of 2.1 mm and which had been cooled to 9 °C at an injection pressure of 100 kg/cm<sup>2</sup>. The temperature of the cylinders C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> were -268 °C, -273 °C and -273 °C, respectively, and the rotational speed of the screw was 80 rpm. The pellets were retained in the extruder for 2.5 minutes. The injection time was 1.5 seconds, and the injection holding time was 9 seconds. Thus, a closed-end parison (total length: 165 mm, outer diameter: 24 mm, inner diameter: 16 mm) was molded. Immediately thereafter the parison was held at 100 °C for 15 seconds. Stretch blow molding (draw ratio by stretching: about 10) was then carried out, whereby a bottle-shaped container having the body portion of 380 $\mu$  thick and a capacity of 1 l was obtained.

#### Comparative Example 1

The dry-blended materials having the same composition as those of Example 1 were blend-pelleted at 280° C by a biaxial extruder (40  $\phi$  ). This blended pellet was used and a stretch blow bottle was obtained under the same molding conditions as in Example 1.

#### Comparative Example 2

The dry-blended materials having the same composition as those of Example 1 were extruded by the same uniaxial extruder in the same way as in Example 1 except in that the residence was 40 minutes, thereby stretch blowing the molded parison, but it was impossible to obtain a uniformly blown product.

#### Comparative Example 3

The dry-blended materials having the same composition as those of Example 1 were extruded by a uniaxial extruder (40  $\phi$  ) with a circular hollow pipe die at 280° C (the residence time in the extruder and die: 4.5 minutes), thereby obtaining a pipe having an outer diameter of 24 mm and an inner diameter of 16 mm. This pipe was cut to form a mouth portion and a bottom by LM-01 and 02 produced by Corpoplast Ltd, so that a parison 165 mm in total length was obtained. The parison was then preheated at 100 to 110° C for 30 minutes by an infrared heater and thereafter it was stretch blown by an LD-01 type stretch blow extruder produced by Corpoplast Ltd, whereby a bottle having the body portion 380 $\mu$  in average thickness and a capacity of 1 l was obtained.

The three kinds of bottles obtained in Example 1, Comparative Examples 1 and 3 were filled with saturated CO<sub>2</sub> water ( O<sub>2</sub> concentration: 0 ppm) so as to be 2 atm at 20° C and were kept at 20° C in an atmosphere of 65 % RH. The concentrations of CO<sub>2</sub> and O<sub>2</sub> were measured by a gas chromatograph and the changes thereof were recorded. The time at which the CO<sub>2</sub> concentration was reduced by 15 % of that of the initial time (hereinunder referred to as "CO<sub>2</sub> 15 % loss") and the time at which the O<sub>2</sub> concentration became 3 ppm (hereinunder referred to as " O<sub>2</sub> concentration 3ppm") were obtained and were made the criteria for the foodstuff preservability. The results are shown in Table 1. Table 1 also shows the results of observation of the wall structures of the containers by a light microscope and an electron microscope. As will be clear from Table 1, the preservation time of the container in accordance with the present invention in terms of CO<sub>2</sub> 15% and O<sub>2</sub> concentration 3 ppm is 2.7 to 3 times those of the containers of blend compositions of Comparative Examples 1 and 3. Further this bottle obtained according to Example 1 had a favorable external appearance and had an excellent strength in drop and pressure resistance.

It is to be noted the preservation time of the container of the present invention is much longer than those of the containers of Comparative Examples 1 and 3. Photos 1 and 2 are micrographs (20,000 x magnification) by a transmission electron microscope of a vertical section and a longitudinal section, respectively, of the body portion of a bottle. It is understood from these photos that the EVOH exhibits a laminar structure consisting of a multiplicity of distinct substantially two-dimensional layers in the matrix of saturated polyester. Many areas (each area is 20 x 20  $\mu$ m) were observed. The average thickness of the layers was 0.001 to 0.03  $\mu$ m, the average aspect ratio was more than 100, and the laminated structural index was more than 30.

According to the photos by an electron microscope (Photo 3 shows a vertical section, and Photo 4 shows a longitudinal section), the EVOHs dispersed in the wall of the container of Comparative Example 1 were flat and particulate, or displayed a lamellar structure 3 to 7 in average aspect ratio and 0.8 to 2.6 in laminated structural index, which was very different from the laminar structure of the container of the present invention. According to the photos by an electron microscope, the EVOHs dispersed in the wall of the container of Comparative Example 3 had configurations similar to those of the EVOHs in Comparative Example 1, and displayed a lamellar structure 2 to 6 in average aspect ratio and 0.8 to 4.4 in laminated structural index, which was very different from the laminar structure of the container of the present invention.

Table 1

Blend Structure	Preservability (week)		Composition of EVOH of Body of Container		Average Aspect Ratio		Laminated Structure Index	
	CO <sub>2</sub> loss 15%	O <sub>2</sub> concentration 3 ppm	Average Thickness $\mu\text{m}$	more than	Vertical Longitudinal Section	more than	Vertical Longitudinal Section	more than
Example 1	90/10	40	35	0.003~0.03	more than	100	more than	30
Comparative Example 1	90/10	15	13	0.03~0.07	3~6	4~7	0.8~2.5	0.7~2.6
Comparative Example 3	90/10	13	11	0.1~0.3	2~5	3~6	0.8~3.8	0.9~4.4

Average Thickness... the average thickness of the EVOH layers on the vertical section and the longitudinal section (section in the diametrical direction) of the body wall of the container in each area (20x20  $\mu\text{m}$ ). (Minimum average thickness to maximum average thickness)

Average Aspect Ratio... the average ratio of the length to the thickness of the EVOH layers on the vertical section and the longitudinal section of the body wall of the container represented by  $l/n \sum_{i=1}^n (l_i/t_i)$  wherein  $l_i$  represents the length of the EVOH layer, and  $t_i$

the thickness thereof in each area (20x20  $\mu\text{m}$ ). (Minimum average ratio to maximum average ratio)

Laminated Structural Index... the average ratio of the distance ( $h_i$ ) between adjacent EVOH layers to the length ( $l_i$ ) of the overlapped portion on the vertical section and the longitudinal section of the body wall of the container represented by  $l/n \sum_{i=1}^n (l_i/h_i)$  in each area (20x20  $\mu\text{m}$ ). (Minimum average ratio to maximum average ratio). Fig. 5 is a schematic view thereof.

Examples 2 to 6

Injection stretch blow containers were obtained in the same way as in Example 1 except for changing

the kinds and the amount of EVOH to be blended. Table 2 shows the results of measurement of the preservabilities and observation of the wall structures. Each of these bottles had a favorable external appearance and had approximately the same strength in drop and pressure resistance as that of the container consisting solely of PET. In addition, each of these bottles displayed high preservability, as shown in Table 2, and is therefore suitable as a container for carbonated beverage.

Table 2

EVOH Et <sup>*1</sup> MI <sup>*2</sup>	Blend Structure PET/EVOH	Preservability (week)		Composition of EVOH of Body of Container			
		CO <sub>2</sub> 15% loss	O <sub>2</sub> Concentration 3ppm	Average Thickness μm	Average Aspect Ratio Vertical Longitudinal Section Section	Laminated Vertical Section Section	Structure Index Longitudinal Section Section
Example 2	44 5	95/5	25	22	0.002~0.2	more than 100	more than 30
Example 3	44 8	80/20	67	58	0.002~0.2	more than 100	more than 30
Example 4	48 8	75/25	69	61	0.001~0.1	more than 100	more than 30
Example 5	17 3	90/10	39	34	0.001~0.1	50~120 more than 100	more than 30
Example 6	33 1	90/10	25	21	0.005~0.5	5~80 10~100	5~20 5~25

\*1 Et: content (mol%) of ethylene unit

\*2 MI: melt index (at 190°C, 2160 g)/(g/10min.)



## Example 7

90 parts of dried pellets (size: 2 x 2 x 4 mm) of poly (ethylene terephthalate/isophthalate) having 6 mol % of isophthalate in monomers of the acid component, and an intrinsic viscosity of 0.82 dl/g and 10 parts of the same pellets of the EVOH as used in Example 1 were dry blended. Thereafter the blend was injected into a mold by the same stretch bottle blower as used in Example 1 under the same conditions as those of Example 1 except that the temperatures of the cylinders C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> were 247°C, 256°C and 256°C, respectively. Thus a bottle-shaped container having a capacity of 1 l was obtained. When this bottle was filled with saturated calcareous water (O<sub>2</sub> concentration: 0 ppm) so as to be 2 atm at 20°C and the preservation term was measured in the above-described way, it showed excellent preservability; the CO<sub>2</sub> 15 % loss was 44 weeks and the O<sub>2</sub> concentration 3 ppm was 37 weeks. Further this bottle had a favorable external appearance and an excellent strength in drop and pressure resistance. The EVOH at the body portion of the bottle exhibited a distinct laminar structure consisting of a multiplicity of substantially two-dimensional layers in the matrix of saturated polyester. The average thickness of the layers was 0.001 to 15 0.1 μm, the average aspect ratio was more than 100, and the laminated structural index was more than 30.

## Claims

- 20 1. An injection stretch blow container comprising a combination of 97 to 70 parts by weight of saturated polyester and 3 to 30 parts by weight of a saponification product of an ethylene-vinyl acetate copolymer, said container having many areas at least at the body wall portion of said container in each of which areas substantially two-dimensional thin layers of said saponification product of said ethylene-vinyl acetate copolymer are laminated in parallel to the wall surface of said container in a matrix of saturated polyester, said saponification product of said ethylene-vinyl acetate copolymer in said area (20 x 20 μm; vertical section or longitudinal section of the body wall of said container) having 0.001 to 1 μm in average thickness and at least 5 in average aspect ratio, and the laminated structural index represented by the following formula being at least 5:
- 30 Laminated structural index

$$I = (1 / n) \sum_{i=1}^n (L_i / h_i),$$

- 35 wherein L<sub>i</sub> represents a length of the overlapped portion of adjacent layers of said saponification product of said ethylene-vinyl acetate copolymer, and  
h<sub>i</sub> represents a distance between adjacent layers of said saponification product of said ethylene-vinyl acetate copolymer.
- 40

2. A container according to Claim 1, wherein said saponification product of said ethylene-vinyl acetate copolymer contains 25 to 60 mol% of ethylene units and the degree of saponification of vinyl acetate unit is at least 96 %.
- 45 3. A container according to Claim 1, wherein said saponification product of said ethylene-vinyl acetate copolymer contains 37 to 50 mol% of ethylene units and the degree of saponification of vinyl acetate unit is at least 96 %.
- 50 4. A container according to any of Claims 1 to 3, wherein said saturated polyester is polyethylene terephthalate.
5. A container according to any of Claims 1 to 3, wherein said saturated polyester is poly (ethylene terephthalate/isophthalate) which contains 2 to 12 mol% of isophthalic acid in a monomer of an acid component.
- 55 6. A container according to any of Claims 1 to 5, wherein said container has many areas at least at the body wall portion of said container in each of which areas substantially two-dimensional thin layers of

said saponification product of said ethylene-vinyl acetate copolymer are laminated in parallel to the wall surface of said container in a matrix of saturated polyester, said saponification product of said ethylene-vinyl acetate copolymer in said area (20 x 20  $\mu\text{m}$ ; vertical section or longitudinal section of the body wall of said container) has 0.001 to 0.2  $\mu\text{m}$  in average thickness and at least 10 in average aspect ratio, and the laminated structural index is at least 15.

7. A container according to any of Claims 1 to 6, wherein the draw ratio of stretch blow is 5 to 20.

## 10 Revendications

1. Conteneur moulé par injection avec soufflage-étirage comportant une combinaison de 97 à 70 parties en poids de polyester saturé et 3 à 30 parties en poids d'un produit de saponification d'un copolymère d'éthylène et d'acétate de vinyle, possédant au moins dans la partie de paroi du corps du dit conteneur de nombreuses zones dans chacune desquelles des couches minces substantiellement bidimensionnelles du dit produit de saponification du copolymère d'éthylène et d'acétate de vinyle sont stratifiées parallèlement à la surface de la paroi du dit conteneur dans une matrice de polyester saturé, le dit produit de saponification du dit copolymère d'éthylène et d'acétate de vinyle dans la dite zone (20 x 20  $\mu\text{m}$ ; section verticale ou section longitudinale de la paroi du corps du dit conteneur) ayant une épaisseur moyenne de 0,001 à 1  $\mu\text{m}$  et un rapport d'aspect moyen d'au moins 5, et l'indice de structure stratifiée représenté par la formule suivante étant au moins égal à 5:
- indice de structure stratifiée

$$I = (1/n) \sum_{i=1}^n (L_i/h_i),$$

où  $L_i$  représente une longueur de portion recouverte de couches adjacentes du produit de saponification du copolymère d'éthylène et d'acétate de vinyle, et

$h_i$  représente une distance entre des couches adjacentes de produit de saponification du copolymère d'éthylène et d'acétate de vinyle.

2. Conteneur selon la revendication 1, dans lequel le dit produit de saponification du dit copolymère d'éthylène et d'acétate de vinyle contient 25 à 60 moles % d'unités éthylène et le degré de saponification de l'unité d'acétate de vinyle est d'au moins 96%.
3. Conteneur selon la revendication 1, dans lequel le produit de saponification du dit copolymère d'éthylène et d'acétate de vinyle contient 37 à 50 moles % d'unités éthylène et le degré de saponification de l'unité d'acétate de vinyle est d'au moins 96%.
4. Conteneur selon l'une des revendications 1 à 3, dans lequel le polyester saturé est du polyéthylène-téréphtalate.
5. Conteneur selon l'une des revendications 1 à 3, dans lequel le polyester saturé est du poly-(éthylèneisophtalate/téréphtalate) contenant 2 à 12 moles % d'acide isophtalique dans un monomère d'un composant acide.
6. Conteneur selon l'une des revendications 1 à 5, dans lequel se trouvent, au moins dans la partie de paroi du corps du conteneur, de nombreuses zones dans chacune desquelles des couches minces substantiellement bidimensionnelles du dit produit de saponification du dit copolymère d'éthylène et d'acétate de vinyle sont stratifiées parallèlement à la surface de la paroi du dit conteneur dans une matrice de polyester saturé, le dit produit de saponification du dit copolymère d'éthylène et d'acétate de vinyle dans la dite zone (20 x 20  $\mu\text{m}$ ; section verticale ou section longitudinale de la paroi du corps du conteneur) possède une épaisseur moyenne de 0,001 à 0,2  $\mu\text{m}$  et un rapport d'aspect moyen d'au moins 10, et l'indice de structure stratifiée est d'au moins 15.
7. Conteneur selon l'une des revendications 1 à 6, dans lequel le rapport de traction de soufflage-étirage

est de 5 à 20.

### Ansprüche

- 5
1. Nach dem Spritzstreckblas-Verfahren hergestellter Behälter mit einer Kombination von 97 bis 70 Gewichtsteilen gesättigtem Polyester und 3 bis 30 Gewichtsteilen eines Verseifungsprodukts eines Ethylen-Vinylacetat-Copolymers, wobei der Behälter viele Bereiche wenigstens im Gehäusewandteil des Behälters aufweist, in jedem der Bereiche im wesentlichen zweidimensionale dünne Schichten des Verseifungsprodukts aus dem Ethylen-Vinylacetat-Copolymer parallel zu der Wandfläche des Containers in einer Matrix von gesättigtem Polyester geschichtet sind, das Verseifungsprodukt des Ethylen-Vinylacetat-Copolymers in der Fläche (20 x 20 µm; senkrechter Abschnitt oder Längsabschnitt der Gehäusewand des Behälters) 0,001 bis 1 µm durchschnittliche Dicke und ein durchschnittliches Streckungsverhältnis von wenigstens 5 aufweist, und der Schichtstrukturindex, der durch die folgende Formel dargestellt wird, wenigstens 5 ist:

$$\text{Schichtstrukturindex } I = (1 / n) \sum_{i=1}^n (L_i / h_i),$$

wobei  $L_i$  eine Länge des Überlappungsteils der angrenzenden Schichten des Verseifungsproduktes des Ethylen-Vinylacetat-Copolymers darstellt, und

$h_i$  einen Abstand zwischen angrenzenden Schichten des Verseifungsprodukts des Ethylen-Vinylacetat-Copolymers darstellt.

2. Behälter nach Anspruch 1, wobei das Verseifungsprodukt des Ethylen-Vinylacetat-Copolymers 25 bis 60 Mol-% Ethyleneinheiten enthält und der Grad der Verseifung der Vinylacetateinheit wenigstens 96 % beträgt.
3. Behälter nach Anspruch 1, wobei das Verseifungsprodukt des Ethylen-Vinylacetat-Copolymers 37 bis 50 Mol-% Ethyleneinheiten enthält und der Grad der Verseifung der Vinylacetateinheit wenigstens 96 % beträgt.
4. Behälter nach einem der Ansprüche 1 bis 3, wobei der gesättigte Polyester Polyethylterephthalat ist.
5. Behälter nach einem der Ansprüche 1 bis 3, wobei der gesättigte Polyester Poly(ethylterephthalat/isophthalat) ist, das 2 bis 12 Mol-% Isophthalsäure in einem Monomer einer Säurekomponente enthält.
6. Behälter nach einem der Ansprüche 1 bis 5, wobei der Behälter mehrere Bereiche wenigstens an dem Gehäusewandteil des Behälters aufweist, wobei in jedem der Bereiche im wesentlichen zweidimensionale dünne Schichten des Verseifungsprodukts des Ethylen-Vinylacetat-Copolymers parallel zur Wandfläche des Behälters in einer Matrix von gesättigtem Polyester geschichtet sind, das Verseifungsprodukt des Ethylen-Vinylacetat-Copolymers in der Fläche (20 x 20 µm; senkrechter Abschnitt oder Längsabschnitt der Gehäusewand des Behälters) 0,001 bis 0,2 µm durchschnittliche Dicke und wenigstens ein durchschnittliches Streckungsverhältnis von 10 aufweist und der Schichtstrukturindex wenigstens 15 ist.
7. Behälter nach einem der Ansprüche 1 bis 6, wobei das Streckungsverhältnis des Streckblasens 5 bis 20 beträgt.

EP 0 218 245 B1

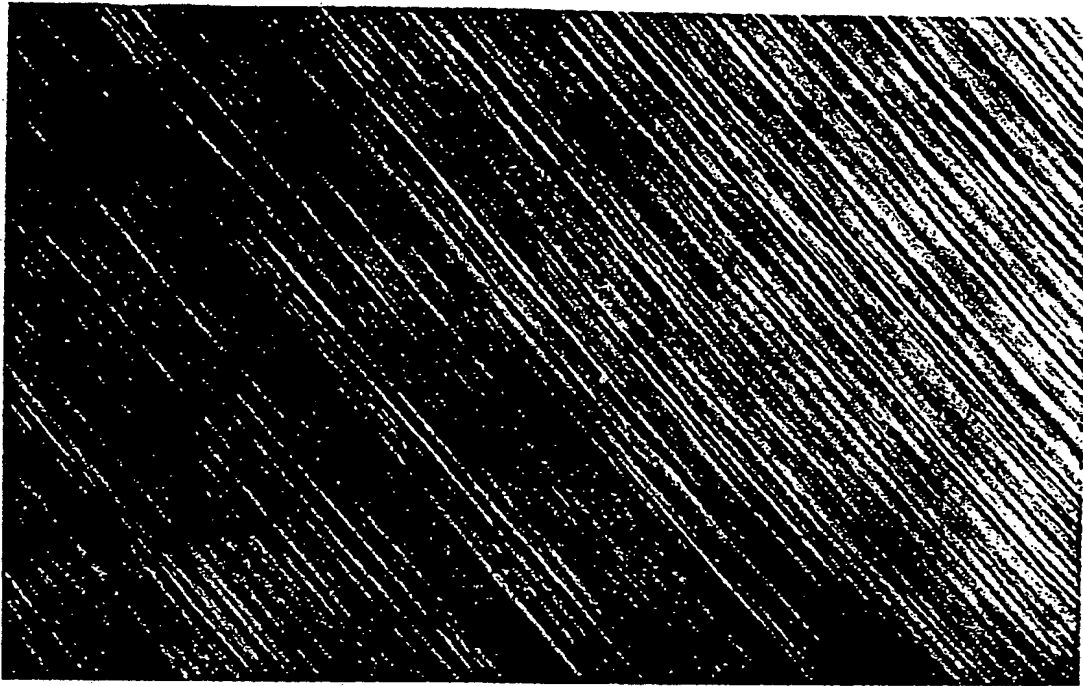


Fig. 2

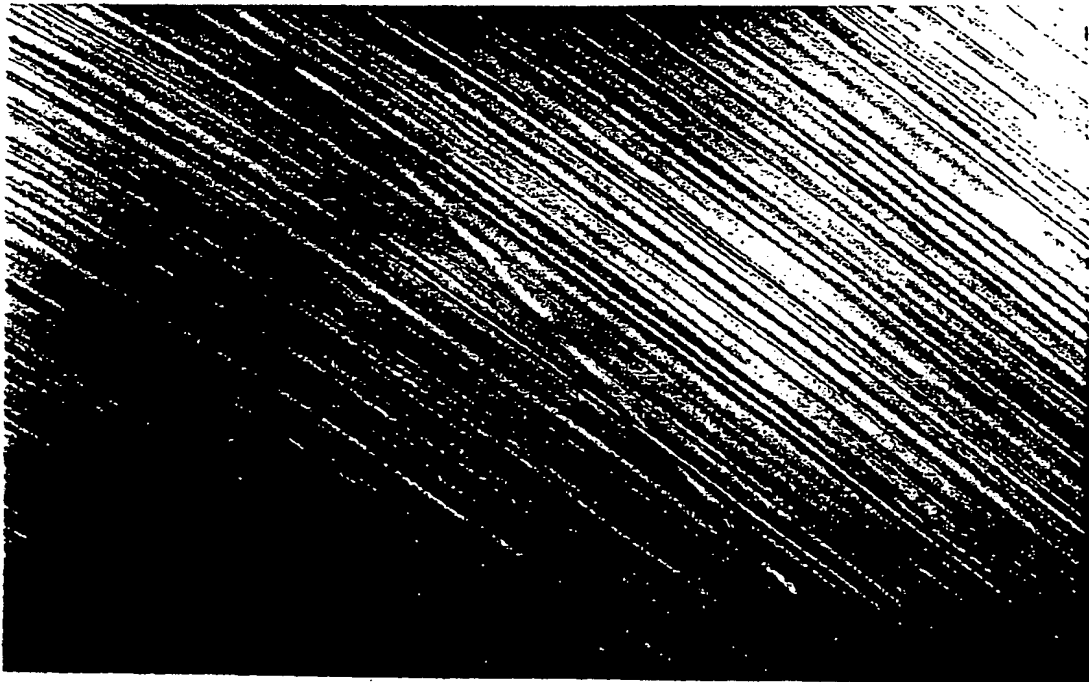


Fig. 3

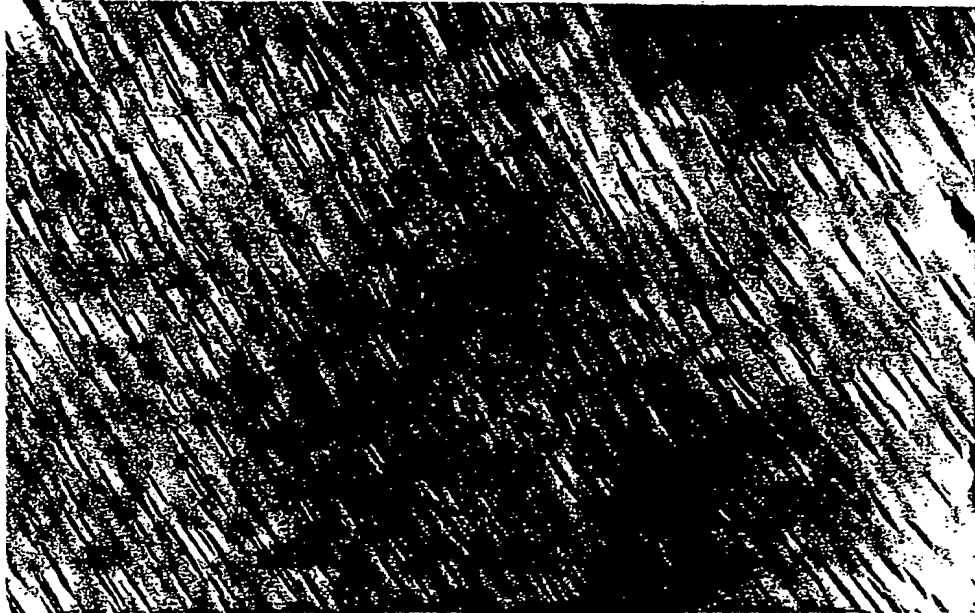
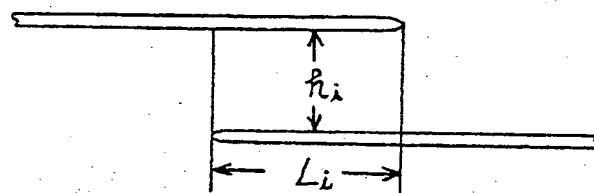


Fig. 4



FIG. 5



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☒ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**